PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01D 53/72, 53/62, B01J 23/00	A2	(11) International Publication Number: WO 97/28887 (43) International Publication Date: 14 August 1997 (14.08.97)

(21) International Application Number: PCT/EP97/00599

(22) International Filing Date: 10 February 1997 (10.02.97)

(30) Priority Data:
BO96A000063 12 February 1996 (12.02.96) IT
BO96A000362 2 July 1996 (02.07.96) IT

(71) Applicants (*for all designated States except US*): CONSIGLIO NAZIONALE DELLE RICERCHE [IT/IT]; Piazzale Aldo Moro, 7, I-00185 Roma (IT). UNIVERSITA' DEGLI STUDI DI BOLOGNA [IT/IT]; Via Zamboni, 33, I-40121 Bologna (IT).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): MATACOTTA, Francesco, Cino [IT/IT]; Via Molini, 22, I-34135 Trieste (IT). CALESTANI, Gianluca [IT/IT]; Via Paullo, 46, I-43100 Parma (IT). CAVANI, Fabrizio [IT/IT]; Via S. Giovanni Bosco, 78, I-41100 Modena (IT). FORNASARI, Giuseppe [IT/IT]; Via Anna Frank, 4, I-26100 Cremona (IT).

(74) Agent: MODIANO, Guido; Modiano & Associati, Via Meravigli, 16, I-20123 Milano (IT).

(81) Designated States: AL, AU, BR, CA, CN, JP, KR, LT, LV, PL, RO, RU, SI, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: CATALYSTS FOR THE FULL OXIDATION OF VOLATILE ORGANIC COMPOUNDS

(57) Abstract

A catalyst for the full oxidation of volatile organic compounds (VOC), particularly hydrocarbons, and of CO to CO_2, which comprises a compound having the formula: $A_2B_3O_{6\pm d}$, where A is an alkaline-earth metal, an alkaline metal, a lanthanide, or a solid solution thereof, B is a transition metal, an element of group III, or a solid solution thereof, and d has a value between 0 and 1; and a method for the full oxidation of volatile organic compounds using the catalyst.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

CATALYSTS FOR THE FULL OXIDATION OF VOLATILE ORGANIC COMPOUNDS

Technical Field

The present invention relates to catalysts for the full oxidation of volatile organic compounds (VOC), particularly hydrocarbons, and to a method for the full oxidation of volatile organic compounds (VOC) by using said catalysts.

Background Art

The total combustion of VOC to CO_2 and H_2O becomes necessary in view of the toxicity and environmental impact of most unburnt VOC. The goal is to minimize both the release of VOC into the atmosphere and the formation of CO, which is also a toxic component.

The catalysts mostly used for VOC combustion are:

a) catalysts based on noble metals, which are characterized by a high cost but by excellent performance in terms of VOC conversion, said catalysts operating at temperatures between 200 and 450^{o}C according to the reactivity of the compound;

b) catalysts based on mixed oxides, typically chromites of copper or of other metals, or barium hexaaluminate, which are characterized by a lower cost but are active in more drastic conditions (temperatures between 400 and 600^{o}C). This second class of catalysts is also used for catalytic combustors for power generation units. In this case, they operate at temperatures above 900^{o}C.

Conventional catalysts used for the combustion of VOC are not free from drawbacks, i.e., high cost (for those based on noble metals) and poor activity (for the second

class, accordingly requiring operation at higher temperatures, in conditions in which morphologic or structural transformations are facilitated).

Disclosure of the Invention

A principal aim of the present invention is to eliminate the drawbacks of conventional catalysts for the oxidation of VOC, particularly catalysts for the full oxidation of VOC.

This aim and other objects which will become apparent hereinafter from the following detailed description of the invention are achieved by catalysts according to the present invention, which comprise one or more crystalline compounds having the formula

$$A_2B_3O_{6\pm d}$$

where A is an alkaline-earth metal, an alkaline metal, a lanthanide, or a solid solution thereof, B is a transition metal, an element of group III, or a solid solution thereof, and d has a value between 0 and 1.

Advantageously, A is chosen from the group constituted by barium, cesium, potassium, strontium, and solid solutions thereof.

Conveniently, B is chosen from the group constituted by copper, nickel, manganese, iron, palladium, titanium, aluminum, gallium, zinc, cobalt, and solid solutions thereof.

Examples of catalysts according to the invention, wherein A is a solid solution of the above-mentioned cations, include compounds having the formula

$(Ba_{2-x}Sr_x)Cu_3O_{6\pm d}$

with values of x up to 0.75.

Other examples of catalysts according to the invention, wherein B is a solid solution of the above-mentioned cations, have the formula

$(Ba_2Cu_{3-y}Pd_y)O_{6\pm d}$

with y up to 0.33;

$Ba_2(Cu_{3-y}Ni_y)O_{6\pm d}$

with y up to 1.0.

Methods for preparing the compounds included in the catalysts according to the present invention are disclosed in Italian patent application BO 96 A 000063. Said patent application describes the use of these compounds to fix gases, composite materials comprising said compounds, films made by said compounds, gas fixing devices comprising said compounds, and electrical and optical gas concentration sensors comprising said compounds.

The catalysts for catalytic combustion according to the present invention are characterized by a high activity, comparable with that provided by the more expensive noble metals, by a high resistance to temperature and to extreme operating conditions, by low cost and easy production even in the form of compounds and thin films. Moreover, differently from any material hitherto known, they are

totally selective for carbon dioxide, CO_2, with respect to carbon monoxide, CO. This means that in any operating condition for the catalysts according to the present invention the only carbon oxide produced by the reaction is CO_2.

The present invention also relates to methods for the full oxidation of VOC which use the catalysts according to the present invention.

The methods for the full oxidation of VOC according to the present invention relate to the full oxidation of VOC in combustion chambers or in afterburning chambers or in combustion-gas chambers.

The oxidation reaction occurs in a fixed bed or in a fluidized bed.

The catalysts according to the present invention lead to full oxidation of VOC. In this manner, the gas mixture produced by the oxidation of the VOC does not contain carbon monoxide but contains only carbon dioxide. In this manner, the operations for eliminating carbon monoxide, and the known negative consequences of its presence in the environment, are avoided. Moreover, by oxidizing the carbon monoxide to carbon dioxide, the full potential of the VOC oxidation reaction is utilized, with obvious advantages in terms of energy.

The Applicants have found that the total VOC oxidation reaction in the presence of the catalysts according to the invention occurs with a high conversion of VOC even at low temperatures.

Moreover, the Applicants have found that the catalysts according to the present invention allow full oxidation of

VOC even in conditions entailing a significant oxygen deficit.

Besides, it has been found that the catalytic activity of the catalysts according to the present invention is not negatively affected by prior heating under reaction up to high temperatures (for example up to 920°C) and cooling to ambient temperature.

Moreover, analysis of reaction selectivity data suggests that the catalysts according to the present invention are capable of directly converting CO to CO_2 at temperatures above 250°C and in the presence of even minimal oxygen concentrations.

The catalysts according to the present invention and the oxidation method according to the present invention will be described in greater detail hereinafter with examples which are presented only by way of non-limitative example.

Example 1

Catalytic combustion of methane

From a molecule-reactivity standpoint, methane is to be considered as difficult to oxidize. The required reaction conditions are extremely drastic if compared with other paraffins, olefins, or volatile organic compounds. Tests that have been conducted have shown that the compound according to the invention is capable of oxidizing methane at relatively low temperatures: this is an indicator of the high full-oxidation ability of the compound according to

the invention. As regards other volatile organic compounds, full combustion is thought to occur at temperatures that are significantly lower than those observed for methane. These indications have been confirmed by the tests conducted with butane and can therefore be extended to the other VOC.

A catalyst containing $Ba_2Cu_3O_6$ was used in tests for the catalytic combustion of methane. The tests are conducted in a fixed-bed quartz microreactor with a diameter of 4 mm, which contains 500 mg of catalysts in granules having dimensions between 20 and 30 mesh. The catalyst is a composite material constituted by an inert porous substrate (Al_2O_3) which contains 3.5% by weight of active compound (17.5 mg). Methane and air are fed to the reactor so that the methane concentration is equal to 2% by volume in the first test and equal to 4% by volume in the second test.

The tests are conducted at atmospheric pressure and at a space velocity, expressed as GHSV (gas hourly space velocity; hourly fed volumetric flow-rate/volume or weight of catalyst), of 80,000 cm^3/g.hour in the first test and of 40,000 cm^3/g.hour in the second test. The mixture of reaction products was analyzed by gas chromatography. The only products formed in both tests were carbon dioxide and water.

The results of the first and of the second tests are given respectively in figures 1 and 2, where the term "conversion" relates to the percentage in moles of converted methane with respect to the moles of supplied methane. The expression "set temperature" relates to the

temperature of the mixture of gases fed to the reactor and the expression "measured temperature" relates to the temperature of the gas mixture at the outlet of the reactor, which is considered equal to the temperature of the catalyst.

Example 2

Combustion test in a thermal cycle

The catalyst according to the example was used in a catalytic methane combustion test carried out in a thermal cycle. The test was conducted in a quartz fixed-bed microreactor with a diameter of 4 mm, which contained 500 mg of catalyst (equal to the catalyst of Example 1) in granules having dimensions between 20 and 30 mesh. Methane and air are fed to the reactor so that the methane concentration is equal to 2% by volume.

The test is conducted at atmospheric pressure and at a space velocity, expressed as GHSV, of 90,000 cm^3/g h. Catalytic activity was analyzed as a function of the temperature and therefore the reaction temperature was increased to 920°C and the catalyst was kept in these conditions for 5 hours. Finally, the system was cooled to 400°C and catalytic activity was analyzed as a function of temperature. The mixture of reaction products was analyzed by gas chromatography. The only products that formed were carbon dioxide and water. The results of the activity tests are given in Table A, where the term "conversion" relates to the percentage of moles of converted methane with

respect to the moles of fed methane.

Table A Test in thermal cycle

Temperature (C)	Conversion 1st cycle (%)	Conversion after 5h at 920°C (%)
400	0	0
450	17	16
500	19	19
550	37	38

At the end of the thermal cycle, activity was unchanged and the discharged catalyst showed a surface area of 116 m^2/g, unchanged with respect to the initial one, which was of 122 m^2/g.

This test demonstrates the good thermal stability of the catalysts used in the present invention.

Example 3

Tests for the combustion of methane in reducing conditions

The catalyst according to the example was used in tests for the combustion of methane in oxygen deficit conditions. The tests were conducted in a fixed-bed quartz microreactor having a diameter of 4 mm, which contained 200 mg of catalyst (equal to the catalyst of Example 1) in granules measuring 20 to 30 mesh. The reactor is fed with

methane and air so that the ratio between methane and oxygen is 2 (vol/vol) in the first test and 5 (vol/vol) in the second test.

The test is conducted at atmospheric pressure and at a space velocity, expressed as GHSV, of 40,000 cm^3/g h. The mixture of the reaction products was analyzed by gas chromatography. The only resulting products were carbon dioxide and water.

The results of the activity tests are listed in figures 3 and 4, where the term "conversion" relates to the percentage of converted methane moles with respect to the fed methane moles.

The complete absence of CO in methane combustion tests conducted in oxygen deficit conditions is particularly significant. The combustion of methane at low temperature and with amounts of oxygen that are well below the stoichiometric ratio generally leads to the formation of incomplete combustion products, such as CO. The complete absence of CO therefore ensures that only full combustion products, such as CO_2 and H_2O, are formed even in drastic conditions and outside the conventional utilization ranges. This result is particularly relevant since with catalysts currently in use it is necessary to operate with an abundant excess of oxygen in order to facilitate combustion to CO_2. The claimed catalysts can operate with a low oxygen/VOC ratio; this makes the conversion efficiency independent of the oxidizing properties of the reaction atmosphere, and this is an undoubtedly advantageous fact.

Example 4

Catalytic combustion of n-butane

The tests were conducted in a laboratory flow reactor operating at atmospheric pressure. 2 g of catalyst, containing 70 mg of $Ba_2Cu_3O_6$ on a porous inert substrate (Al_2O_3) with particles having a diameter of about 0.5 mm, are loaded. A mix constituted by n-butane (1.7% molar) in air is fed so as to provide a contact time (expressed as ratio between the catalyst volume and the volumetric feed flow-rate measured in normal conditions) which can vary between 0.7 and 4.4 seconds (results shown in Table B), or a contact time set to 4.4 seconds and a temperature that can vary between 320 to 480°C (results shown in Table B). The n-butane ignition temperature can be extrapolated from the table data and is between 280 and 300°C.

Table B. Oxidation of n-butane

Contact time (s)	Temperature (°C)	Conversion to $n\text{-}C_4H_{10}$ (%)
0.7	340	18
1.5	340	32
2.2	340	39
2.9	340	45
3.6	340	51
4.4	340	55

4.4	320	42
4.4	340	55
4.4	360	62
4.4	380	70
4.4	400	77
4.4	420	86
4.4	440	94
4.4	460	100

Total lack of carbon monoxide in the combustion products, constituted exclusively by H_2O and CO_2, is observed.

Table B lists the values of the percentage conversion of n-butane (reacted moles/fed moles) and the yield in CO_2 (produced moles of CO_2/(supplied moles of n-butane*4)). The experimental characteristics of this example reduce conversion efficiency with respect to the examples given for methane oxidation. Laminar flow and limitation by self-diffusion of the reaction products in fact penalize the efficiency, which nonetheless remains very high.

The catalysts according to the present invention and the total VOC oxidation method according to the present invention can be used with good results for gaseous organic compounds or for organic compounds that vaporize at low temperature, achieving complete combustion at low temperature. The CO_2 selectivity of the catalysts according to the present invention is a unique characteristic. The oxidation of VOC, particularly hydrocarbons with catalysts that are not specific for combustion, usually leads to the formation of both CO and CO_2. Both products are

thermodynamically facilitated in the conditions normally used, and their ratio is therefore usually conditioned by kinetic factors. Accordingly, the specificity of the catalyst in the formation of CO_2 is linked to the characteristics of the active centers. CO_2 is in fact a primary product, as demonstrated by tests conducted by varying the contact time, and therefore is not the result of the intermediate formation of CO. It is also fair to assume that primary carbon monoxide, i.e., the carbon monoxide that is not produced by the partial oxidation of VOC, is efficiently converted to carbon dioxide at temperatures above 250^{o}C and in the presence of low oxygen concentrations.

The catalysts according to the present invention and the process for the full oxidation of gaseous organic compounds can be used to reduce or eliminate many noxious components from the combustion gases generated in any manner, for example from very large scale facilities for generating electric power down to small combustors for domestic use, including important applications in the engine field and in the field of vehicles with internal-combustion engines.

The selectivity of the CO_2 yield also makes the use of the catalysts according to the present invention particularly interesting in combustors for closed spaces (gas stoves, water heaters for sanitary use, cooking devices, etcetera) where the presence of CO in the combustion products is notoriously a serious health hazard.

CLAIMS

1. A catalyst for the full oxidation of volatile organic compounds (VOC), particularly hydrocarbons, and of CO to CO_2, comprising a compound having the formula

$A_2B_3O_{6\pm d}$

where A is an alkaline-earth metal, an alkaline metal, a lanthanide, or a solid solution thereof; B is a transition metal, an element of group III, or a solid solution thereof; and d has a value between 0 and 1.

2. A catalyst according to claim 1, characterized in that A is chosen from the group constituted by barium, cesium, potassium, strontium, a lanthanide, and solid solutions thereof.

3. A catalyst according to claim 1, characterized in that B is chosen from the group constituted by copper, nickel, manganese, iron, palladium, titanium, aluminum, gallium, zinc, cobalt, and solid solutions thereof.

4. A catalyst according to claim 1, characterized in that said compound has the formula $Ba_2Cu_3O_{6\pm d}$.

5. A catalyst according to claim 1, characterized in that said compound has the formula

$(Ba_{2-x}A_x)Cu_3O_{6\pm d}$

where A is an alkaline or an alkaline-earth metal or a lanthanide.

6. A catalyst according to claim 1, characterized in that said compound has the formula

$(Ba_{2-x}Sr_x)Cu_3O_{6\pm d}$, $0 < x < 0.75$.

7. A catalyst according to claim 1, characterized in that said compound has the formula

$Ba_2(Cu_{3-y}B_y)O_{6\pm d}$, $0 < y < 1$

where B is a transition metal or an element of group III.

8. A catalyst according to claim 1, characterized in that said compound has the formula

$Ba_2(Cu_{3-y}Ni_y)O_{6\pm d}$, $0 < y < 1$

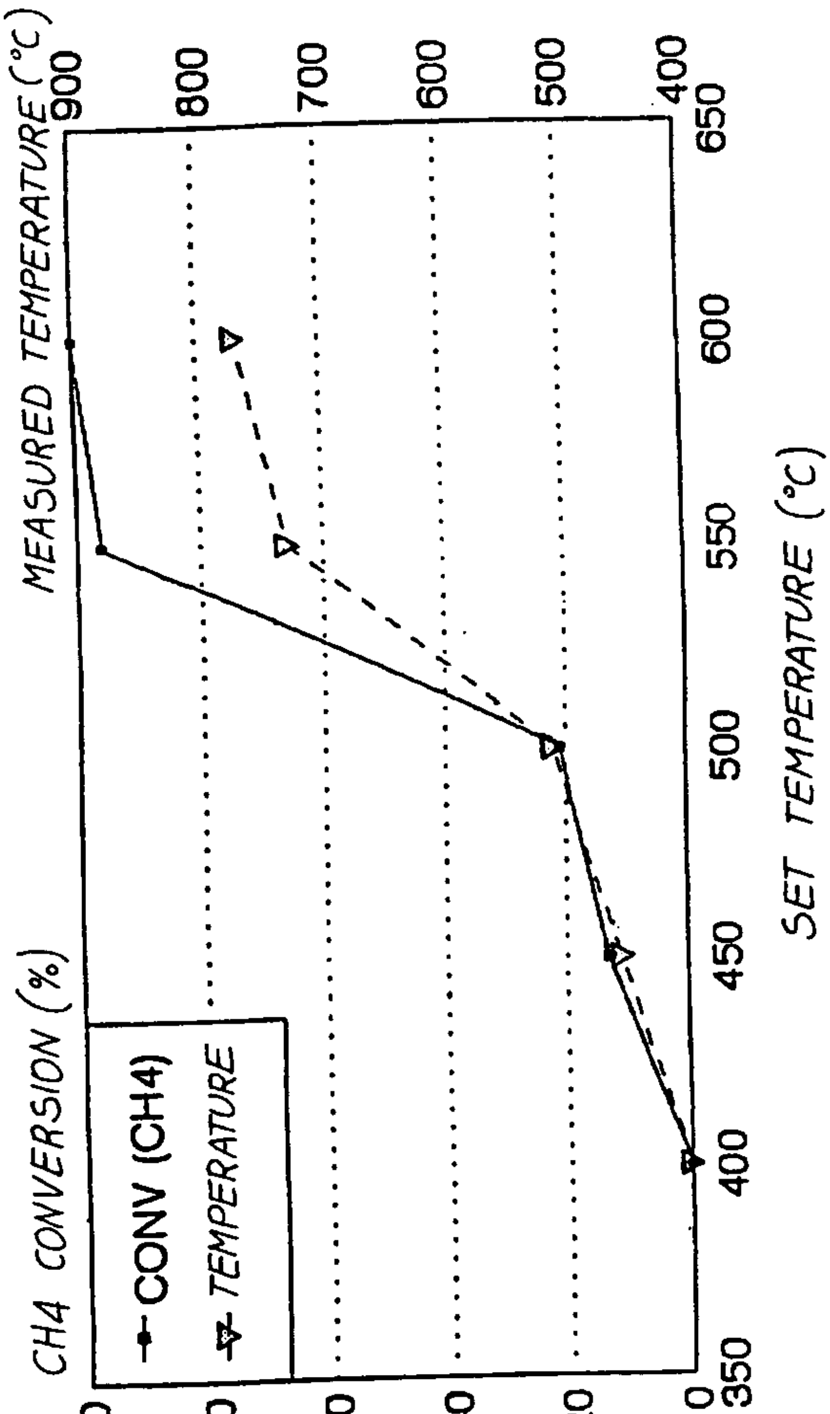
9. A catalyst according to claim 1, characterized in that said compound has the formula

$Ba_2(Cu_{3-y}Pd_y)O_{6\pm d}$, $0 < y < 0.33$

10. A composite catalyst constituted by one or more catalysts according to claims 1 to 9, supported in any manner on other materials, both inert and functional, in the form of composite material or thin film.

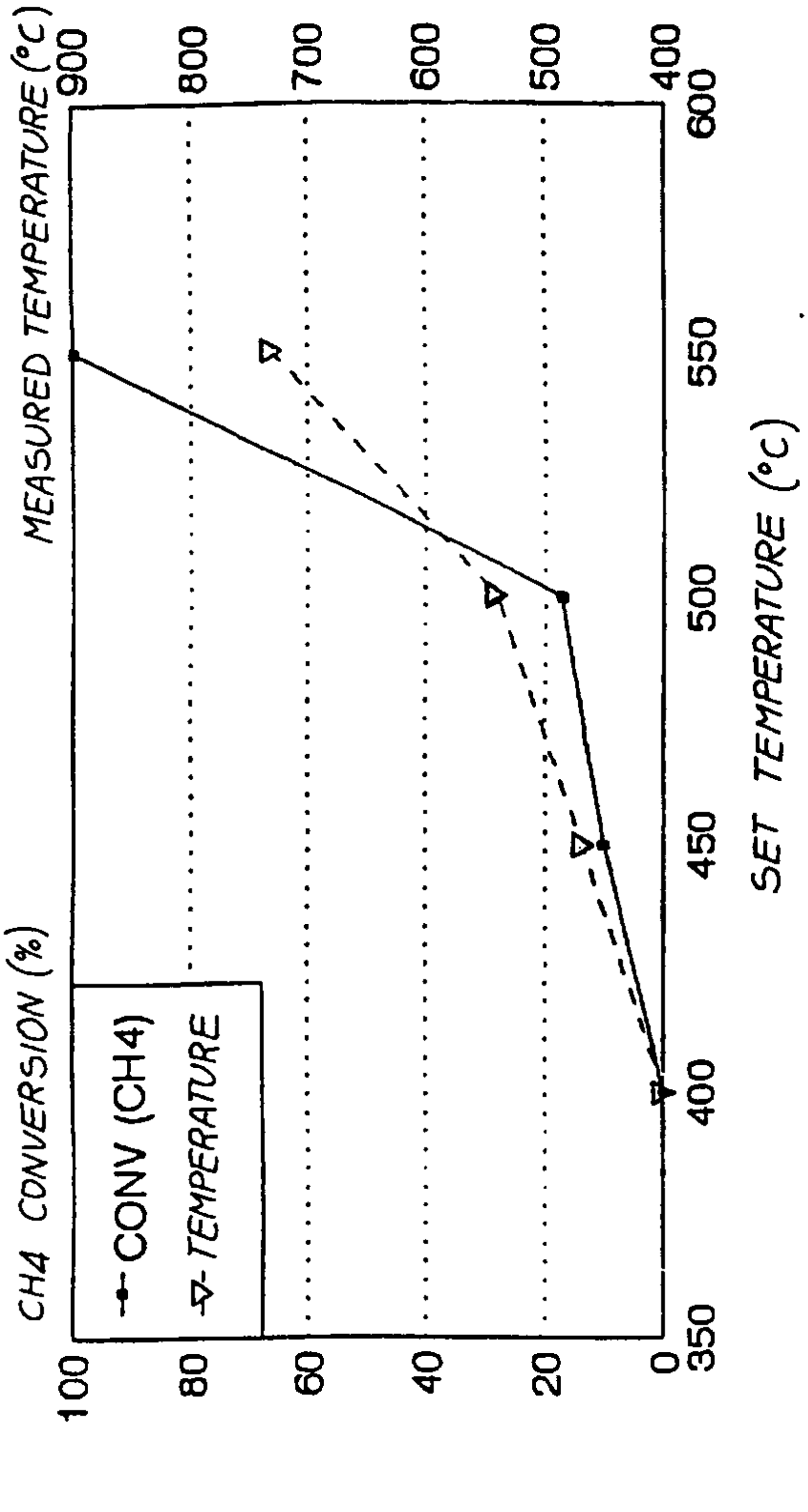
11. A method for the full oxidation of volatile organic compounds, particularly hydrocarbons, characterized in that a catalyst according to one of claims 1 to 10 is used.

12. A method for converting carbon monoxide to carbon dioxide, characterized in that a catalyst according to claims 1 to 10 is used.



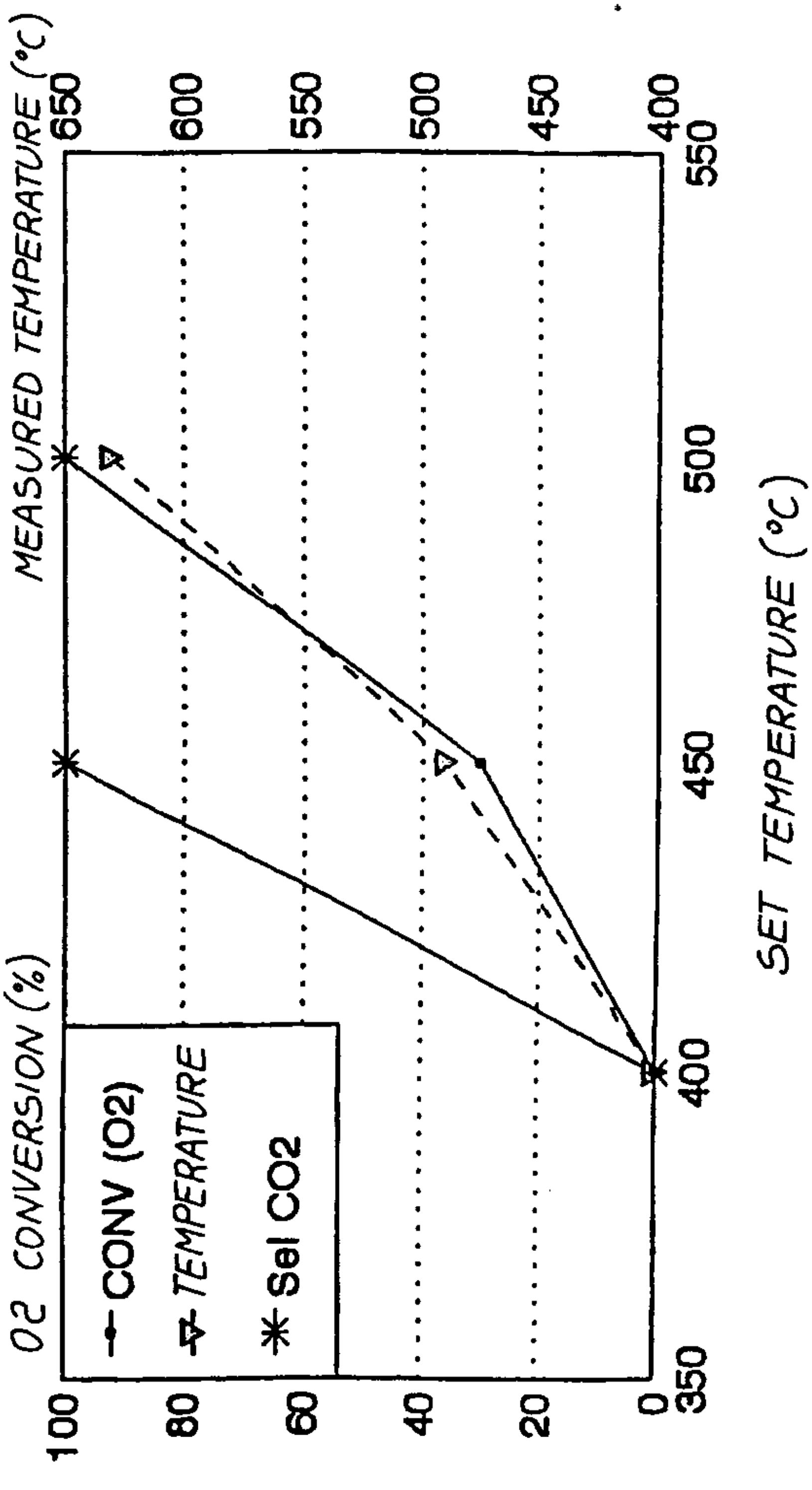
GHSV=80000 CH4/Air =2/98 v/v

Fig. 1



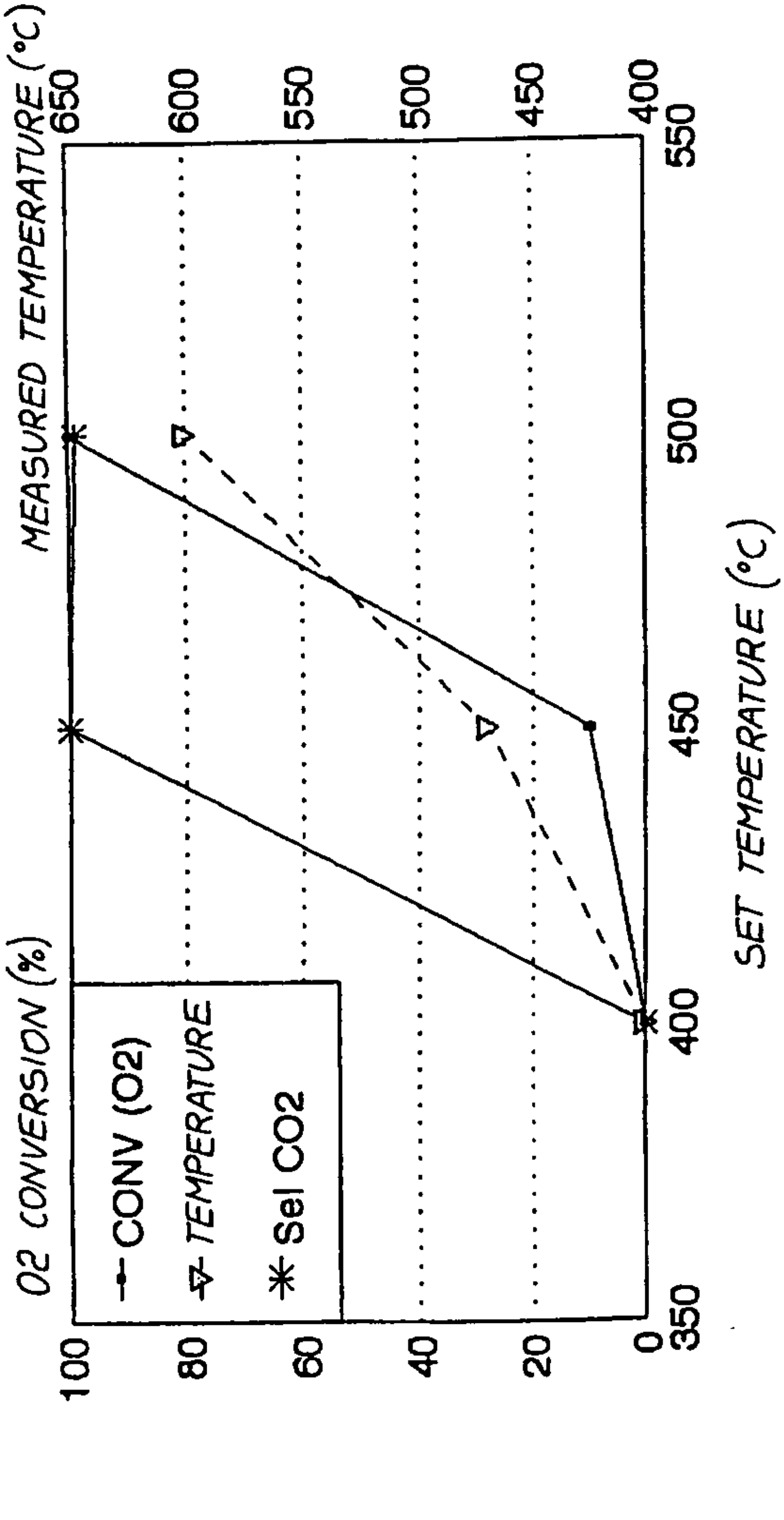
GHSV=40000 CH4/Air =4/96 v/v

Fig.2



GHSV=40000 CH4/O2/He=2/1/4 v/v

Fig. 3



GHSV=40000 CH4/O2/He=5/1/4 v/v

Fig. 4